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Treatability Studies of Pesticide Manufacturing Wastewaters: Dinoseb and Atrazine

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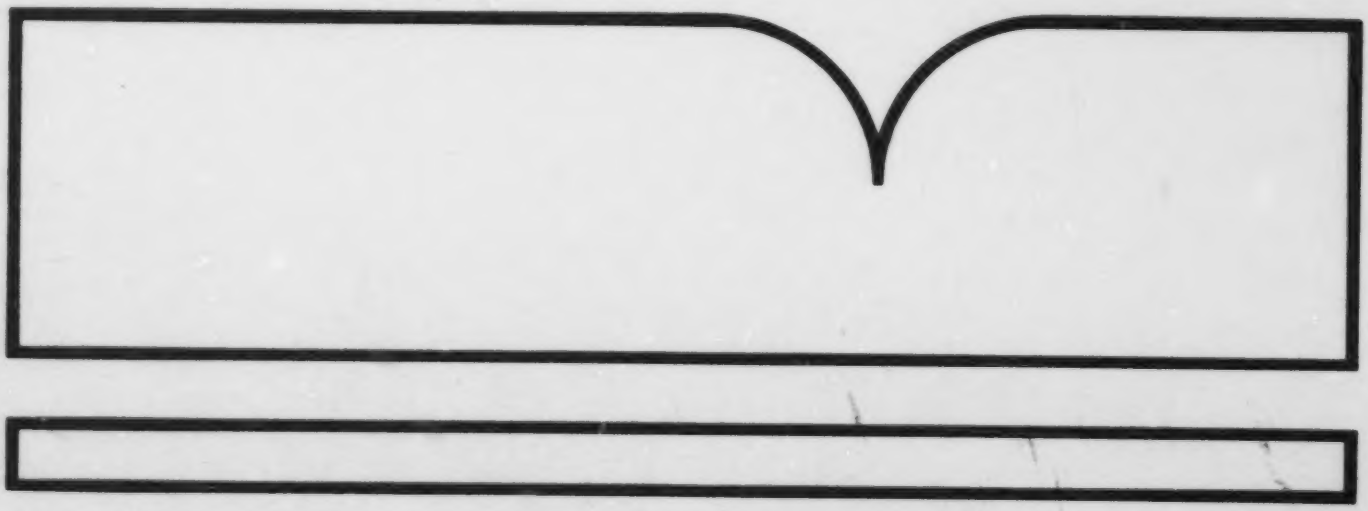

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Waste Water	Dinoseb	
Water Treatment	Atrazine	
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TREATABILITY STUDIES OF PESTICIDE MANUFACTURING WASTEWATERS: DINOSEB AND ATRAZINE

by

Edward Monnig
Ruth A. Zweidinger
Research Triangle Institute
Post Office Box 12194
Research Triangle Park, North Carolina 27709

Contract No. 68-02-2688

Project Officer

David C. Sanchez
Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, North Carolina 27711

OFFICE OF ENVIRONMENTAL ENGINEERING AND TECHNOLOGY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ABSTRACT

Laboratory and pilot studies of the treatability of pesticide manufacturing wastewaters were conducted in a project designed to investigate the suitability of individual pesticide manufacturing wastewaters for discharge to biological treatment systems, whether publicly owned treatment works (POTW) or on-site systems.

Aqueous effluents from the manufacture of dinoseb and atrazine were evaluated in a hierarchical approach in which the least costly treatment was evaluated first. Using this approach a combination of preliminary activated carbon filtration to remove pesticides followed by biological treatment to reduce oxygen demand due to other organics was found effective. Other treatments found inadequate were dilution with municipal wastewater and biological treatment and chemical pretreatment to hydrolyze the pesticide followed by biological treatment.

Activated carbon filtration alone greatly reduced the phytotoxicity of the pesticide wastewater even though substantial breakthrough of some organic compounds occured.

This report was submitted in partial fulfillment of Contract No. 68-02-3688 by the Research Triangle Institute under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period May 1, 1979 to July 31, 1979 and work was completed August 31, 1979.

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SECTION 1

INTRODUCTION

In February 1979 Research Triangle Institute (RTI) was requested by the Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP) of the U.S. Environmental Protection Agency (EPA) to conduct laboratory and pilot studies of the treatability of pesticides manufacturing wastewaters. The project is designed to investigate the suitability of individual pesticide manufacturing wastewaters for discharge to biological treatment systems, whether publicly owned treatment works (POTW) or on-site systems.

The approach taken with each pesticide manufacturing wastewater is hierarchial in nature; that is, less costly, more available methods of treatment are investigated first. The preferred method of treatment is assumed to be biological treatment. If the pesticide is judged suitable to biological treatment based on chemical and toxicological evaluation of the waste before and after treatment, additional options are not investigated.

If pesticide manufacturing wastewater disrupts biological treatment systems, the possibility of pretreating the waste prior to biological treatment is investigated. Pretreatment options may include pH adjustments, filtration, flocculation, oxidation and others depending on the nature of the waste and its chemical composition.

If pretreatment does not make the waste compatible with activated sludge systems, adsorption techniques may be investigated. These may include both carbon and resin systems. The necessity for physical-chemical pretreatment of wastewaters will again be evaluated as with the biological treatment system.

This report details a study of the treatability of wastestreams resulting from the manufacture of dinoseb and atrazine products by Vertac, Inc. at their Vicksburg, Mississippi plant.

SECTION 2

CONCLUSION AND RECOMMENDATIONS

The effluent from the manufacture of dinoseb and atrazine proved suitable for a treatment system involving preliminary activated carbon filtration to remove the herbicide followed by biological treatment to reduce oxygen demand exerted by solvents and other organic compounds. Several other treatment systems were tried but did not prove successful. These alternatives included biological treatment of the manufacturing wastes diluted in municipal wastewater. This system provided some reduction in chemical oxygen demand (COD) of the waste. However, both the dinoseb and the atrazine levels were unaffected.

A pretreatment system involving the hydrolysis of pesticide manufacturing wastes was attempted. This system greatly reduced the phytotoxicity of the wastes as measured by the algal bioassay. However, subsequent biological treatment of this waste provided only a marginal reduction in the hydroxyatrazine byproducts of the hydrolysis reaction.

Activated carbon filtration alone greatly reduced the phytotoxicity of the pesticide manufacturing wastes. Substantial breakthrough of other organic compounds (i.e. solvents such as acetone) was seen before any breakthrough of either of the pesticides from the carbon column. This COD content was then further reduced in a biological treatment system through the mechanisms of volatilization and biological degradation. Biological treatment reduced the phytotoxicity of these wastes beyond that seen with activated carbon treatment alone.

The volatile nature of the organic constituent of this waste could allow consideration of air stripping as a viable treatment option after carbon treatment. Additional work would be necessary to determine the effluent quality achievable with air stripping and the nature of the stripped organics.

A report has been made of the formation of nitrosamines in excess of 200 ppm in the formulation of dinoseb as a diethanolamine salt (Bontoyan, Law, and Wright, 1979). While the formulation of dinoseb at the Vertac facility is not expected to generate an aqueous wastestream, care should be taken in any washup or rinsing procedure after formulation. Monitoring for various nitroamines is recommended if there is reason to believe that there is a source of input of these nitrosamines into the main plant wastestream.

SECTION 3

SELECTED LITERATURE REVIEW: DINOSEB

GENERAL CHEMICAL INFORMATION

Chemical Names

2-sec-butyl-4,6-dinitrophenol; 2-(1-methyl-n-propyl)-4,6-dinitrophenol; 2,4-dinitro-6-sec-butylphenol.

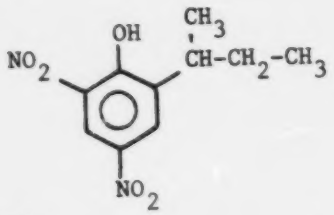
CAS Number

88-85-7

Synonyms and Trade Names

DNBP, DNSBP, DNOSBP, CHEMOX®, Gebatox®, Premerge®, Knox Weed®, Sinox General®, Supersevtox®.

Structure



Introduced

A patent was assigned to Dow Chemical in 1946 for use of dinoseb as a general contact weed killer for both pre and post emergence control (Lane, 1967).

Manufacture

The 2,4-dinitro-6-alkylphenols can be prepared by sulfonation of 6-alkylphenol with concentrated sulfuric acid. This product is then dissolved in water and sufficient nitric acid added to convert the sulfonic acid derivative to the desired nitrophenol (Sittig, 1977).

Current Waste Disposal Practices

Wastes from dinoseb manufacture at the Vertac facility are presently treated with activated carbon to remove herbicide content.

Dow Chemical was assigned a patent (3,844,914) for the photolytic purification of dinoseb. This process involves acidifying solutions of the compound to pH $\leq$ 3.5 and irradiating by ultraviolet light in either a continous or a batch process. This process is said to reduce 100 ppm solutions to less than 1 ppm. Sparging with oxygen increases decomposition rates. Energy requirements range from 200-500 kilowatt hours per pound of compound.

ECOLOGICAL EFFECTS

Table 1 summarizes the published ecological effects data from dinoseb.

TABLE 1. ECOLOGICAL EFFECTS DATA FOR DINOSEB

Species	Test Duration	Result (LC_{50}[a])	Reference
Yearling Channel Catfish (Ictalurus punctatus)	96 hour	0.118 mg/L	McCorkle, Chambers and Yarbrough (1977)
Mosquitofish (Gambusia affinis)	96 hour	0.87 mg/L	Fabacher and Chambers, (1974)
Crayfish (Orconectes limosus)	144 hour	>10.0 mg/L	Zitko, McLeese, Carson, and Welch (1976)
Lobster, Larvae (Homarus americanus)	0.3 hour	1.0 mg/L	Zitko, McLeese, Carson, and Welch (1976)
Lobster, Adults	3.0 hour	1.0 mg/L	Zitko, McLeese, Carson, and Welch (1976)
Cutthroat Trout (Salmo clarki)	96 hour	0.041 mg/L at pH 6.5	Woodward (1976)

TABLE 1 (Continued)

Species	Test Duration	Results (LC_{50}[a])	Reference
Cutthroat Trout	96 hour	1.35 mg/L at pH 8.5	Woodward (1976)
Lake Trout (*Salvelinus namaycush*)	96 hour	0.032 mg/L at pH 6.5	Woodward (1976)
Lake Trout	96 hour	1.4 mg/L at pH 8.5	Woodward (1976)
Lake Trout, Fry	60 days	<0.0049; >0.010 mg/L	Woodward (1976)
Speckled Trout (*Salvelinus fontinalis*)	96 hour	0.11 mg/L	Christie and Penny (1972)
Japanese quail (14 days old)	8 days	409 ppm in feed	Hill, Heath, Spann, and Williams (1975)
Ring-necked pheasant (10 days old)	8 days	515 ppm in feed	Hill, Heath, Spann and Williams (1975)
Mallard (10 days old)	8 days	540 ppm in feed	Hill, Heath, Spann, and Williams (1975)
Algae (*Chlorella pyrenoidos*)	24 hour	1.0 mg/L	Hawxby, Tubea, Ownby, and Baslery (1977)
Scud (*Gammarus fasciatus*)	96 hour	1.8 mg/L	Sanders (1970)

[a] LC_{50} refers to the concentration lethal to 50% of the test population in the specified time.

Dinoseb is a relatively toxic pesticide. Of the eighteen herbicides studied by McCorkle et al. (1977) (including alanap, bensulfide, chloramben, 2,4-D acid, 2,4-D dimethyl amine salt, dalapon, diuron, DSMA, EPTC, fluometuron, metribuzin, monuron, MSMA, nitralin, propanil, 2,4,5-T and trifluralin) the herbicides dinoseb, trifluralin, and bensulfide were the most toxic to fingerling catfish. These three herbicides were several orders of magnitude more toxic than the other herbicides tested (Table 1 for dinoseb), though their toxicity was less than that of endrin (96 hr LC_{50} of endrin for fingerling catfish ~ 0.001 mg/L). Pravda (1973) found that dinoseb was the most toxic of the 14 herbicides studied to the roundworm Tubifex sp., the crustaceans Daphnia pulex and Gammarus pulex, and the fish Perca fluviatilis. Woodward (1976) found that concentrations of dinoseb as low as 0.5 µg/L effected the ability of trout fry to absorb the yolk sac. These data would indicate the need for caution in the application of the herbicide dinoseb around aquatic environments.

ENVIRONMENTAL FATE IN SOILS

Doyle, Kaufman and Burt (1978) found that the evolution of ring-labeled ^{14}C from dinoseb applied to the soil at a rate of 2 ppm ranged from 18% to 36% of the total over a 60 day incubation period. When dinoseb was provided as the only organic source it was found to be degraded 90% in 20 days by pure cultures of Pseudomonas aeruginosa and 50% in 20 days by pure cultures of P. putida (Douros and Reid, 1956). Dinoseb was not found to effect soil microbial activity as assayed by CO_2 evolution and dehydrogenase activity when applied at recommended rates (Lewis, Papavizas, and Hora, 1978). Even when applied at concentrations 100 times higher than recommended rates these authors report that dinoseb was not found to effect alfalfa decomposition. Dinoseb at these concentrations did reduce algal populations in the soil by more than 90% (Lewis, et al., 1978).

Health Effects

An extensive review of the mode of action and metabolic effects of phenolic herbicides is provided by Kaufman (1975). The mechanism of the toxic action of dinoseb in mammalian species is based on uncoupling of oxidative phosphorylation.

The LD_{50} for oral administration of dinoseb to rats is reported to be 50 mg/kg (Dalgaard-Mikkelsen and Poulsen, 1962). The dermal LD_{50} to guinea pigs is reported to be approximately 150-300 mg/kg (Wolfe, Durham, and Batchelor, 1961). Dinoseb has been reported as non-mutagenic in tests with histidine-requiring mutants of Salmonella typhimurium (Andersen, Leighty, and Takahashi, 1972).

While few difficulties might be expected with dinoseb itself, a report of potential hazard in dinoseb formulations must be noted. Dinoseb is most often sold in formulations of amine salts (alkanolamine salts of the ethanol and isopropanol series). High concentrations of nitrosamines, potent animal carcinogens, have been reported in the diethanolamine salt of dinoseb (Bontoyan, Law and Wright, 1979). Specifically, diethanolnitrosamine was found at concentrations greater than 200 mg/L in this dinoseb formulation. The mechanism and source of formation of the nitrosamines is not known at present (personal communication, W. R. Bontoyan). Additional work is critical to pinpoint this source of nitrosamines.

SECTION 4

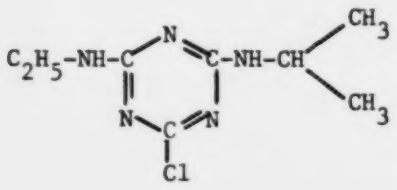
SELECTED LITERATURE REVIEW: ATRAZINE*

GENERAL CHEMICAL INFORMATION

Pesticide: Atrazine CAS No. 1912-24-9

Gesaprim™; Aatrex™; Atrasol™; G-30027

Structure



2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine

Chemical Category

Triazine; other triazines include simazine, propazine, cyprozine, terbuthylazine, cyanazine, prometone, secbumetone, terbumetone, desmetryn, ametryn, prometryn, metoprotryn, terbutryn, aziprotryn, dimethametryn, dipropetryn.

Properties

Colorless crystals, m.p. 173-175 C; v.p. 3.0 x 10^{-7} mm Hg at 20 C. (Martin and Worthing, 1974). pKa (21 C) = 1.7; density of 1.187 g/cm^3 (Esser et al., 1975). Soluble in 2% alcohol. Solubility in water at 20-25

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*Literature review taken from Little, L. W., R. A. Zweidinger, E. C. Monnig and W. J. Firth, Treatment Technology for Pesticide Manufacturing Effluents: Atrazine, Maneb, MSMA, and Oryzalin. EPA-600/2-80-043, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1980. 277 pp.

C is 33 mg/l (Esser et al., 1975), with the atrazine dissolving according to a first order reaction, the solubility and rate constant increasing with temperature (Calvet et al., 1975). The activation energy of solubilization is approximately 4.1 - 4.8 kcal/mole, i.e., there is a 30% decrease in time required for 50% solubilization when the temperature increases by 10 C (Calvet et al., 1975). Sol. in methanol, 18,000 mg/l; in chloroform, 52,000 mg/l (Martin and Worthing, 1974). Stable in neutral, slightly acidic, or basic media, but hydrolyzed to the herbicidally inactive hydroxy derivative by alkali or mineral acids at higher temperatures; non-corrosive (Martin and Worthing, 1974). Undergoes photodecomposition with ultraviolet light in aqueous solution to form the 2-hydroxy analogs (Esser et al., 1975); acetone may serve as a photosensitizer (Burkhard and Guth, 1976).

Intended Use

Herbicide. Registered in 1958 as a herbicide. Used as selective pre- and post-emergence herbicide on numerous crops, including corn, sorghum, sugar cane, and nursery conifers (Martin and Worthing, 1974). Recommended for use in fish ponds for selective control of farm pond weeds, especially submerged aquatics (Johnson, 1965).

Mode of Action

Taken up by roots or foliage; inhibits growth of most plant organs; at subtoxic levels may increase chlorophyll content, and resistant crops may be a darker green; inhibits photosynthesis within photosystem II at the stage where water is photolysed; inhibits respiration; causes pollen cell abnormalities in pollen cells of grain sorghum, but has no effect on yield (Brian, 1976). Little if any effect on structure of chloroplast of the green alga Chlorella ellipsoidea, but causes degradation of chloroplasts of barnyard grass; does not affect mitochondria at up to 20 ppm; causes chromosomal aberrations in several plants (Linck, 1976). Inhibits photosynthetic CO_2 fixation but does not affect dark fixation of CO_2 in corn, cotton, and soybeans (Frans et al., 1972).

Manufacture Information

Amount Produced Annually: 49.9×10^3 metric tons in 1974 (Archer et al., 1978)

Manufacturers	Locations
Ciba-Geigy	St. Gabriel, LA
Missouri Chemical Company	St. Joseph, MO
Vertac, Inc.	Vicksburg, MS

According to a recent farm periodical, "Big Farmer" (Anon. 1977), other companies either make or formulate atrazine products since atrazine products are listed as being available from Monsanto, Dow, Stauffer, Drexel, and Shell companies.

Atrazine has the largest use volume of any pesticide in the United States.

Health and Ecological Effects

Toxicity--

Oral, LD_{50}, rat, 2000 mg/kg (Weber, 1977); 3080 mg/kg (Martin and Worthing, 1974).

Mouse, 1750 mg/kg (Martin and Worthing, 1974).

Acute dermal LD_{50}, rabbit, 7500 mg/kg (Martin and Worthing, 1974).

Not tumorigenic to the mouse at 10-22 mg/kg/day (Hayes, 1975).

LD_{50}, fish, 12.6 mg/L (Weber, 1977).

Toxic to the carp Cyprinus corpio L. at 35 mg/L and to the trout Salmo irideus at 5-30 mg/1 (Lüdemann and Kayser, 1966)

Toxic at levels as low as 3 ppm to fry of the fish Coregonus fera (Gunkel and Kausch, 1976).

Toxic to daphnia at approximately 20 mg/L (< 50% killed) (Lüdemann and Kayser, 1966).

With Daphnia magna and Moina rectirostris, at 1 ppm over 30-45 days increases duration of embryonic and postembryonic development, as well as decreases number of broods and number of offspring per brood. (Shcherban, 1973).

Limiting value for tubifex worm, 300 mg/L (Lüdemann and Kayser, 1966).

Atrazine at nontoxic levels acts synergistically with certain insecticides, such as carbofuran, DDT, parathion, and diazinon, to significantly enhance their toxicity to the fruit fly (Lichtenstein et al., 1973).

Fate in Soils--

Half-life in soil, 26-78 weeks (Weber, 1977); may be adsorbed by components such as montmorillonite (Calvet, Tercé, and Renard, 1975).

Effect on nitrification in the soil is unresolved, as both stimulatory and inhibitory effects have been noted (Greaves et al., 1976).

Atrazine treatment of soils does not affect subsequent crops of sensitive species if residuals are <0.13 mg/L (Fusi and Franci, 1972).

Atrazine at 10^{-3} concentration produced no evidence of mutagenic influence on the haploid flowering plant Pelargonium (Pohlheim et al., 1977).

Monitoring of several major U. S. rivers and tributaries indicated that atrazine is detectable year round, at values generally less than 1 ppb; no nitrosoatrazine was found in the samples (Newby and Tweedy, 1976).

Mutagenic Potential--

Atrazine alone produces no mutagenic effects in the usual short-term tests for mutagenicity. For example, there is no effect on Tradescantia hair cells and no evidence of cytogenetic activity on root tips of Hordeum, Vicia, and Sorghum vulgare (Müller et al., 1972). At 10^{-3} M concentration, it produces no evidence of mutagenicity in the haploid flowering plant Pelargonium (Polheim et al., 1977). However, it does induce genetic alterations in maize germ cells and extracts from atrazine-treated maize do show mutagenic activity (Plewa, and Gentile, 1976). Extracts from maize kernels treated with 5 and 20 ppm increased mitotic gene conversion in the yeast Saccharomyces cerevisiae by (respectively) 2.5 and 4 times over controls, whereas a 100 mg/L solution of atrazine alone had no effect; even greater activity was found in leaf extracts

(18-30 times over controls) leading to speculation as to the food chain effect (Plewa and Gentile, 1976).

Manufacturing Process

Atrazine may be prepared by reaction of cyanuric chloride with one equivalent of ethylamine followed by one equivalent of isopropyl amine in the presence of an acid-binding agent (Sittig, 1977). The charts shown below represent idealized schemes. They do not necessarily represent individual plants, which vary somewhat in production processes.

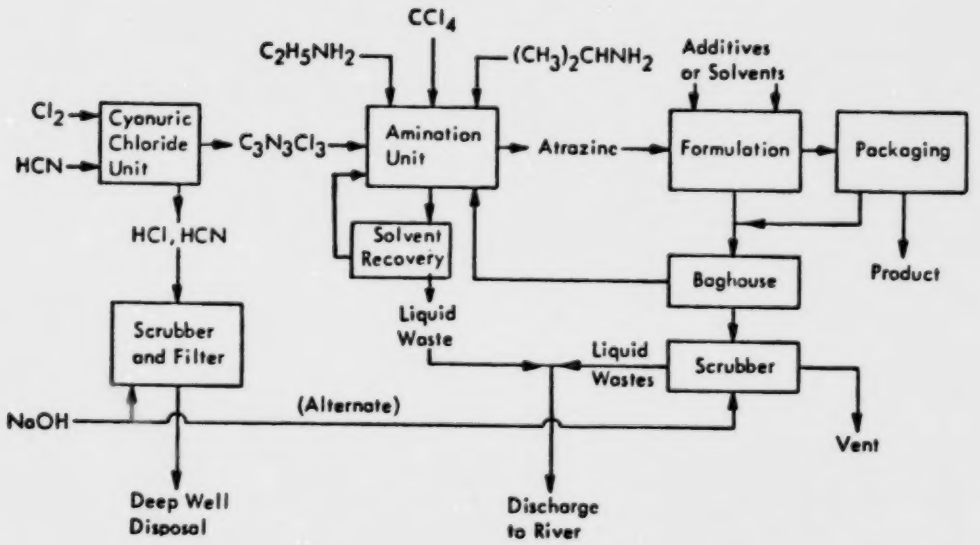


Figure 1. General production and waste scheme for atrazine. By Permission from M. Sillig in Pesticide Process Encyclopedia. Noyes Data Corporation, Park Ridge, N.J., 1977.

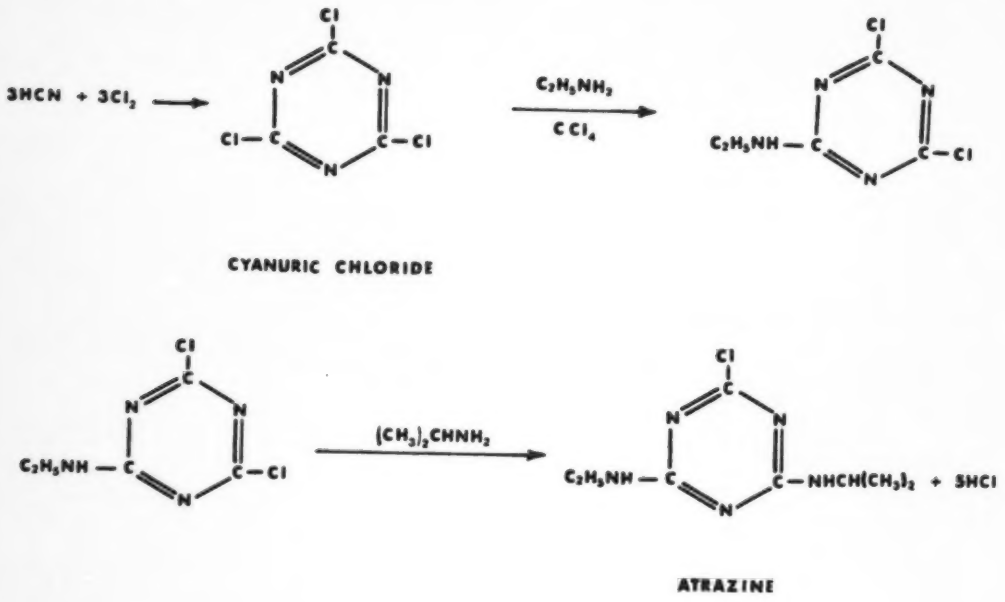


Figure 2. General chemistry of atrazine production (Sittig, 1977).

SECTION 5

TREATABILITY STUDIES

CHARACTERIZATION OF WASTEWATER FROM DINOSEB AND ATRAZINE MANUFACTURING PROCESS

Two wastestreams were sampled in connection with this treatability study. Input to the first wastestream was comprised of the supernatant remaining after the dinoseb manufacturing process (batch). This stream is a highly concentrated corrosive waste comprised of 21% sulfuric acid which is subsequently neutralized with either sodium hydroxide or ammonium chloride. A grab sample of waste from a typical batch was neutralized to pH 7 with sodium hydroxide (50%) for use in this study.

Table 2 presents selected wastewater parameters for the dinoseb supernatant wastestream (see Appendices A and B for methods of analysis). The total dissolved solids and the dinoseb concentrations present in this waste would prevent biological treatment without substantial dilution.

The second wastestream sampled in this study receives wastewater from three sources: effluent from the atrazine manufacture, specifically the distillation residual remaining after solvent recovery and filtration of atrazine; wash water and ground runoff from dinoseb manufacture; and non point storm water runoff. This wastestream (dinoseb-atrazine composite) provides the bulk of the volume of wastewater flow from this facility.

A composite 20 gallon sample was taken of this wastestream over a 24 hour period using an Isco interval sampler set for 10 minute intervals. Intermittent but heavy thunderstorms which are typical of this region of the country were experienced during a 6 hour portion of the sampling period. The runoff during these storms greatly increased the flow rate in the effluent lines for a period during and after rainfall. However, analysis of the four, five-gallon subsamples which made up the 20 gallon composite sample showed little difference in dinoseb or atrazine concentrations (see Table 3).

TABLE 2. PESTICIDE MANUFACTURING WASTEWATER CHARACTERIZATIONS

Parameter	Dinoseb Supernatant*	Dinoseb-Atrazine Composite
pH	7.0	2.5
Cl^-, mg/L	15,000	1,250
Acidity, mg/L as $CaCO_3$ to pH 6.0	ND	230
Total Kjeldahl Nitrogen, mg/L	-	100
Ammonia, mg/L as N	-	100
Oxidized Nitrogen, mg/L as N	-	50
Total Phosphorus, mg/L	-	0.75
Chemical Oxygen Demand, mg/L	14,500	960
Total Dissolved Solids, mg/L	280,000	2,800
Settleable Solids, mL/L	1.0	Trace
Dinoseb, mg/L	750	4.05
Atrazine, mg/L	ND	28.4

*Several parameters could not be measured on this waste due to interferences.

TABLE 3. PESTICIDE CONCENTRATIONS IN VARIOUS FRACTIONS OF THE DINOSEB-ATRAZINE COMPOSITE SAMPLE

	Atrazine (mg/L)	Dinoseb (mg/L)
Fraction 1	26.4	3.5
Fraction 2	30.0	4.75
Fraction 3	25.2	5.0
Fraction 4	32.0	3.5

Table 2 presents selected wastewater parameters for the dinoseb-atrazine composite sample. Several comments on the parameters given in Table 2 for the dinoseb-atrazine sample should be made. The measured value of total Kjeldahl nitrogen (TKN) should be at least slightly higher than the ammonia levels presented since there is organic nitrogen present in the atrazine molecule. However, the digestion procedure for the TKN determination is not effective for the ring-bound nitrogen of aromatic compounds.

The COD levels in this composite sample dropped during the 2.5 month study period from 960 mg/L to 750 mg/L. This drop probably represents the volatilization of organics during the handling of these samples. The manufacturer reports the widespread use of acetone at this facility. As will be noted below in the discussion of treatment options, volatile compounds appear to comprise a major portion of the COD of this waste stream.

The pH of this wastestream is too low for biological treatment without adjustment. However, the buffer capacity of this wastestream as represented by the acidity measure would not require a large amount of base to raise the pH to biologically acceptable levels. Approximately 4.7 millequivalents of NaOH per liter of waste were required to raise the pH to 7.

TREATABILITY STUDY: BIOLOGICAL TREATMENT

An initial attempt was made to biologically treat a mixture of the dinoseb supernatant and dinoseb-atrazine composite. These wastes were mixed in a ratio of 1 part dinoseb supernatant to 49 parts dinoseb-atrazine composite which is the approximate proportion in which these wastes are generated

at the manufacturing facility. Fifty mL of the combined pesticide waste mixture was then diluted to a liter with settled municipal wastewater. The pH of this wastewater was raised to 7.0 - 7.5 and buffered with 0.4 g/L of $NaHCO_3$.

As a control for the possible interferences of atrazine wastewater on the degradation of dinoseb a second condition was run. One mL of dinoseb supernatant was diluted to one liter with settled municipal wastewater without the addition of dinoseb-atrazine composite. Wastewater was buffered as above.

These final mixtures were then fed to two pair of bench scale activated sludge (AS) units as described in Appendix C. Retention time in the AS units was 8 hours. Mixed liquor volatile suspended solids (MLVSS) was initially determined to be 2000 - 2200 mg/L. Dissolved oxygen in the aeration section of the units was maintained at a minimum of 3 mg/L.

It was initially hoped that the concentrations of dinoseb and atrazine wastes used in the influent to the AS units could be gradually increased as the system acclimated to these wastes. Such optimism was not warranted. Seventeen days of operation showed no increase in the system's ability to degrade the pesticides even at these low concentrations in the influent. Dinoseb concentrations in the influent and effluents of both test conditions remained at 0.8 mg/L. The atrazine concentration remained at 1.0 mg/L in both the influent and effluent of the units fed dinoseb-atrazine composite.

COD reduction was noted during this phase in the treatability study. Table 4 presents this data for both sets of units. As can be seen the COD

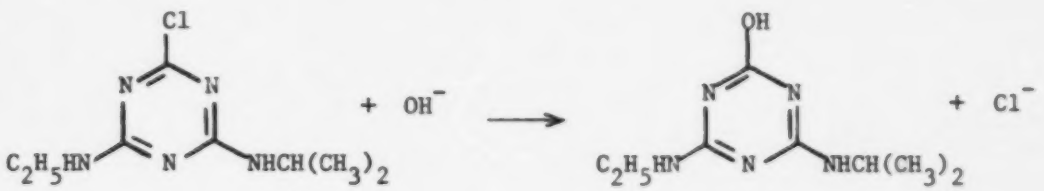
TABLE 4. COD LEVELS IN INFLUENT AND EFFLUENT FROM ACTIVATED SLUDGE UNITS

	Dinoseb Supernatant Feed	Dinoseb-Atrazine and Dinoseb Supernatant Feed
Average Influent COD (mg/L)	146	171
Average Effluent COD (mg/L)		
Unit 1	48	63
Unit 2	45	56
Reduction	69%	64%

reductions was appoximately 66%. However, given the lack of reduction in pesticide concentration during activated sludge treatment, this system was not seen as a viable option for reducing the pesticide concentrations to a level required by the manufacturer's discharge permit.

TREATABILITY STUDY: HYDROLYSIS, CARBON TREATMENT, AND BIOLOGICAL TREATMENT

It has been reported that hydrolysis of atrazine under conditions of high pH and temperature will result in the production of hydroxyatrazine by direct nucleophilic substitution of an hydroxide ion for a chloride ion as shown below (Shih and Dal Porto, 1975).



The two possible advantages were seen in hydrolyzing atrazine. First, hydroxyatrazine is reported to be herbicidally inactive (Kaufman and Blake, 1970). Second, a major degradation pathway of atrazine in the soil results in the formation of hydroxyatrazine as an intermediate (Harris, 1967). There is some disagreement in the literature concerning the formation of hydroxyatrazine as a rate limiting step in the environmental degradation of atrazine. Harris (1967) reported the accumulation of hydroxyatrazine in soils treated with atrazine. On the other hand Skipper and Volk (1972) reported a 25 to 40 times faster evolution of ring-labeled ^{14}C from hydroxyatrazine as compared with atrazine after soil applications of each compound. In the present study it was hypothesized that preliminary hydrolysis of atrazine waste would provide for a more rapid cleavage of the ring during activated sludge treatment.

The atrazine-dinoseb composite was pretreated by raising the pH to 14, refluxing the sample at 100°C for 3 hours, and readjusting the pH to 7. Table 5 presents data on the approximate rate of hydrolysis of atrazine and the fate of the hydrolysis products. As can be seen the hydrolysis of

TABLE 5. HYDROLYSIS OF DINOSEB-ATRAZINE WASTE

Reflux time (min)	Atrazine, mg/L	Hydroxyatrazine, mg/L
0	22.4 ± 1.2	5.5 ± 0.2
30	17.3 ± 0.3	8.4 ± 0.3
60	2.6 ± 0.3	24.2 ± 0.2
90	0	24.2 ± 0.2
120	0	24.7 ± 0.1
150	0	24.7 ± 0.1
180	0	24.6 ± 0.1
210	0	24.7 ± 0.1
240	0	24.7 ± 0.1
270	0	24.7 ± 0.1

TABLE 6. EFFECT ON ALGAL GROWTH OF DINOSEB-ATRAZINE WASTEWATER (UNTREATED)

Wastewater (mL/L)	0.01	0.1	1.0	10
Growth (% of control on Day 14)	76	75	76	6.4

TABLE 7. EFFECT ON ALGAL GROWTH OF DINOSEB-ATRAZINE WASTEWATER (HYDROLYZED)

Wastewater (mL/L)	0.1	1	10	100
Growth (% of control on Day 14)	76	89	99	67

atrazine at pH 14 and 100°C is completed within 90 minutes. Continued refluxing does not effect the stability of hydroxyatrazine. Heating is critical for rapid hydrolysis of atrazine. Merely raising the pH to 14 did not result in hydrolysis of atrazine at room temperature over a 16 hour period.

Hydrolysis of the atrazine-dinoseb composite had little effect on the dinoseb concentration. Dinoseb concentration before pH treatment was 3.0 mg/L and after pH treatment was 2.9 mg/L.

Reduction in COD from approximately 840 mg/L to 250 mg/L was noted after the refluxing. Again this reduction probably represents the loss of volatile compounds during the refluxing process.

To test for reduction in herbicidal properties of this waste, an algal assay was run comparing the dinoseb-atrazine composite waste before and after hydrolysis (method: Appendix D). As can be seen in Tables 6 and 7 the EC_{50} for untreated wastewater was between 1.0 and 10 ml/L and the EC_{50} for hydrolyzed wastewater was greater than 100 ml/L.

Based on the failure of the previous attempt to treat dinoseb by biological treatment it was decided to pretreat the dinoseb supernatant waste with activated carbon to remove the dinoseb. Since the dinoseb supernatant would represent the largest contribution of dinoseb to any treatment system, treatment of this wastestream before dilution could provide an efficient treatment system. Specifically under some circumstances the amount of dinoseb absorbed onto a given mass of carbon has been reported to be a function of concentration of dinoseb in the treated stream, though competition from other more absorbable compounds in a multisolute system can disrupt this relationship (Carnahan, 1973).

Filtered dinoseb supernatant (Whatman 2V) was treated by passage through a column 2.5 cm in diameter and filled to a height of 142 cm with a slurry of 360 g (dry weight) of carbon. Bed volume of this column was 697 mL and the flow rate was 13 mL/min (0.63 gal/ft^2/min). Three liters of dinoseb supernatant were passed through the column. The first bed volume collected from the column was discarded. No dinoseb was detected in any of the subsequent three liters collected from the column. A sizeable reduction in COD was also noted in the carbon treated effluent as seen in Table 8.

TABLE 8. COD OF CARBON TREATED DINOSEB SUPERNATANT WASTE

Sample	COD (mg/L)
Dinoseb Waste Whatman 2V Filtered	13,700
Carbon Filtered (Liter 1)	2,500
Carbon Filtered Waste (Liter 2)	3,400
Carbon Treated Waste (Liter 3)	3,800

A shift in coloration was noted in the dinoseb supernatant waste. Prior to carbon treatment its color at pH 7 was a dark brown and at pH 4 the waste had the intense yellow color characteristic of nitrophenols. After carbon treatment the waste was a blue-green color similar to that of copper sulfate although atomic absorption analyses showed only traces of copper (<1 mg/L). The intensity of color increased with successive fractions. Absorbance readings were taken of the eluent on a Perkin-Elmer Ultraviolet-Visible spectrophotometer, Model 402. Significant end absorption was noted below 250 nm. An additional absorbance peak was noted at 300 nm. Absorbance readings of the various fractions at a wavelength of 300 nm and 1 cm path length were as follows: liter 1, 2.95; liter 2, 3.78; liter 3, 3.93, calculated from measurements on dilutions of these fractions. Operation and performance parameters of a pilot carbon system tested at Vertac for treating dinoseb supernatant are given in Appendix E.

Carbon treated dinoseb supernatant was mixed with hydrolyzed dinoseb-atrazine composite in ratio of 1:49. This mixture was then diluted to 10% in settled municipal wastewater, buffered with 0.4 g/L of $NaHCO_3$, and subjected to activated sludge treatment under the conditions presented above with the following changes. Two AS units were maintained at a 20 hour retention time and two AS units were maintained at a 48 hour retention time. An additional two units were run on settled municipal wastewater alone as controls at a 20 hour retention time.

The test units were fed 10% pesticide wastewater for 7 days. The pesticide wastewater was then increased in increments of 15% for the subsequent two weeks and increased to 60% on week 4. At this point the experiment was discontinued due to lack of significant degradation of hydroxyatrazine (Figure 3).

Gradual loss of sludge was noted in all test units during the 4 week test period with the loss being greatest in the 48 hour units. Reduction in MLVSS was 25% in 24 hour test units, 70% in 48 hour test units, and 10% in the controls. Several factors can account for this drop in MLVSS. The extended aeration mode of operation with its lower food to microorganism ratio will result in a drop in sludge production as the bacterial population shift further into endogenous respiration. Additional difficulties with poorly settling sludges resulting in carry-over of solids in the effluent have been noted in extended aeration modes. The addition of pesticides and other wastes with toxic characteristics can increase this problem. Increased solids were noted in the effluent of the test units as compared to controls. The solids contributed to the increased COD of the test unit effluents as shown in Figures 4 and 5.

TREATABILITY STUDY: CARBON PRETREATMENT, BIOLOGICAL TREATMENT

Given the previous failures of attempts to biologically degrade atrazine, dinoseb and their analogs within the constraints of activated sludge systems, it was decided to lower the pesticide concentration with carbon filtration. Biological treatment would then be used to reduce the levels of any residual organics which broke through the carbon filter prior to pesticide breakthrough.

A column 2.5 cm in diameter was filled to a height of 45 cm with a slurry of 100 grams (dry weight) of carbon. The bed volume of this column was 221 mL. Dinoseb-atrazine composite waste (pH unadjusted) was pumped through this column at a rate of 13 mL/min (0.63 gal/ft^2/min).

A total of 105 bed volumes (23.2 L) was pumped through the column. No dinoseb or atrazine was detected at any point in the effluent from the carbon column. The rise in COD levels with increasing bed volumes followed a sigmoid pattern as presented in Figure 6. The COD of bed volumes 81-105 was approximately that of the untreated sample.

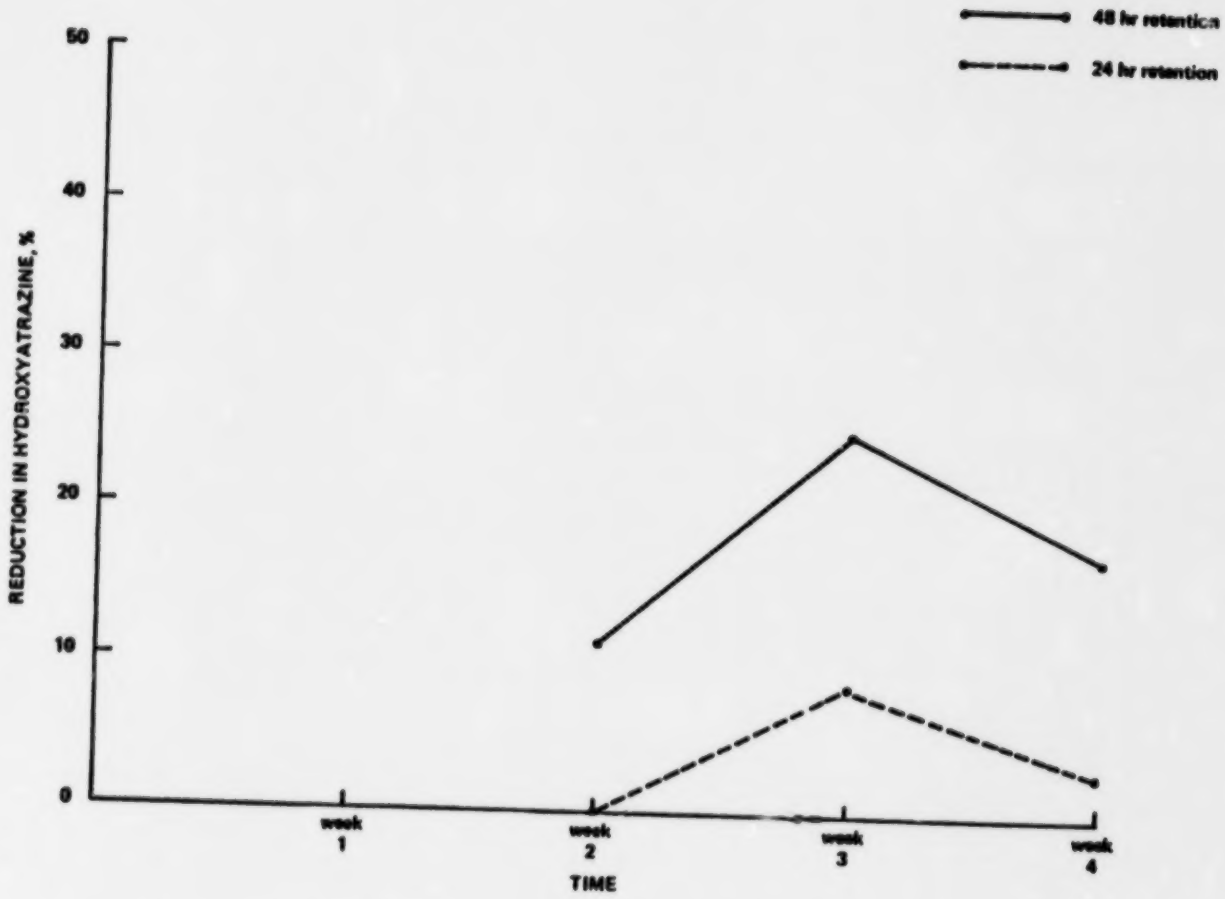


Figure 3. Reduction in effluent hydroxyatrazine through biological treatment.

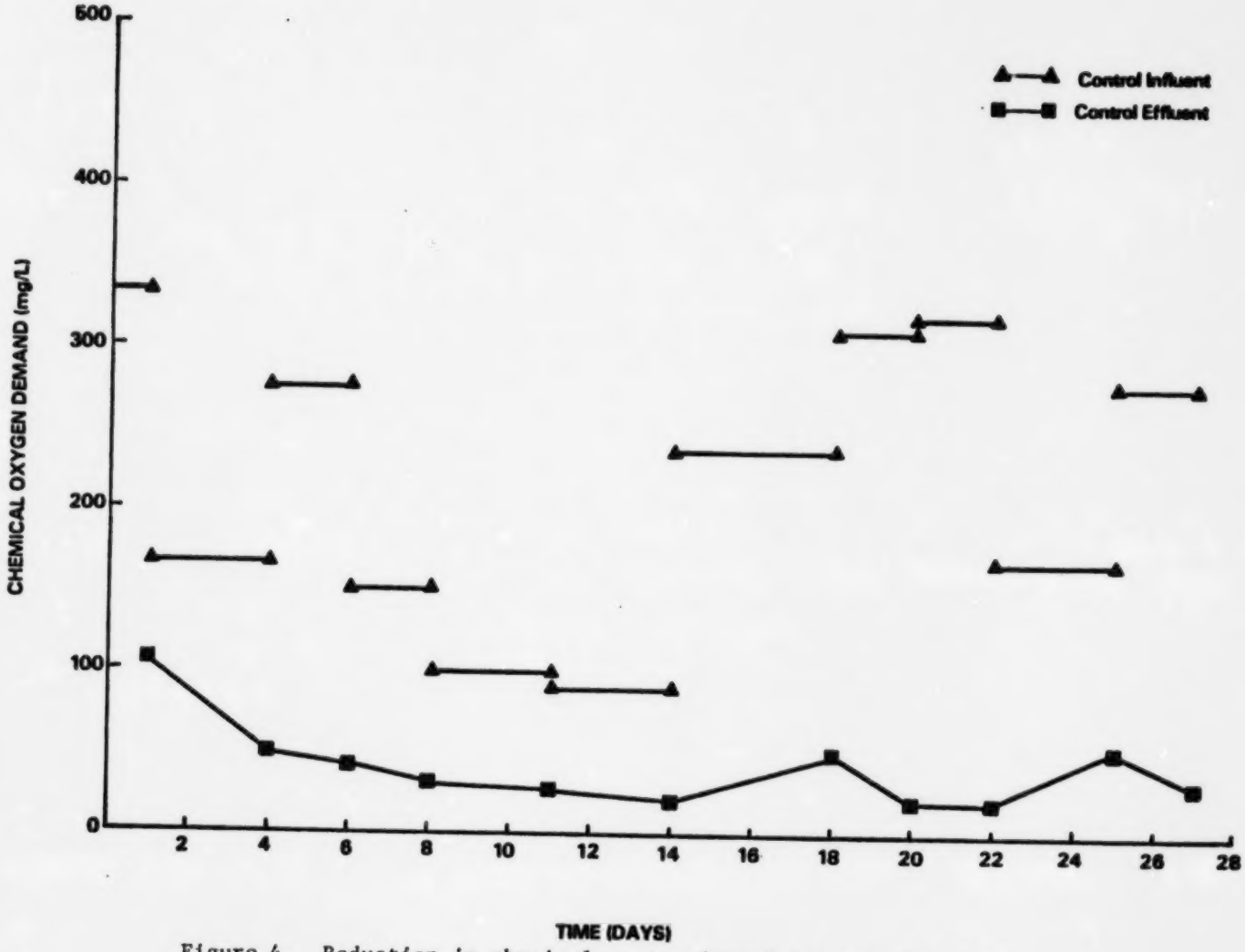


Figure 4. Reduction in chemical oxygen demand in control units.

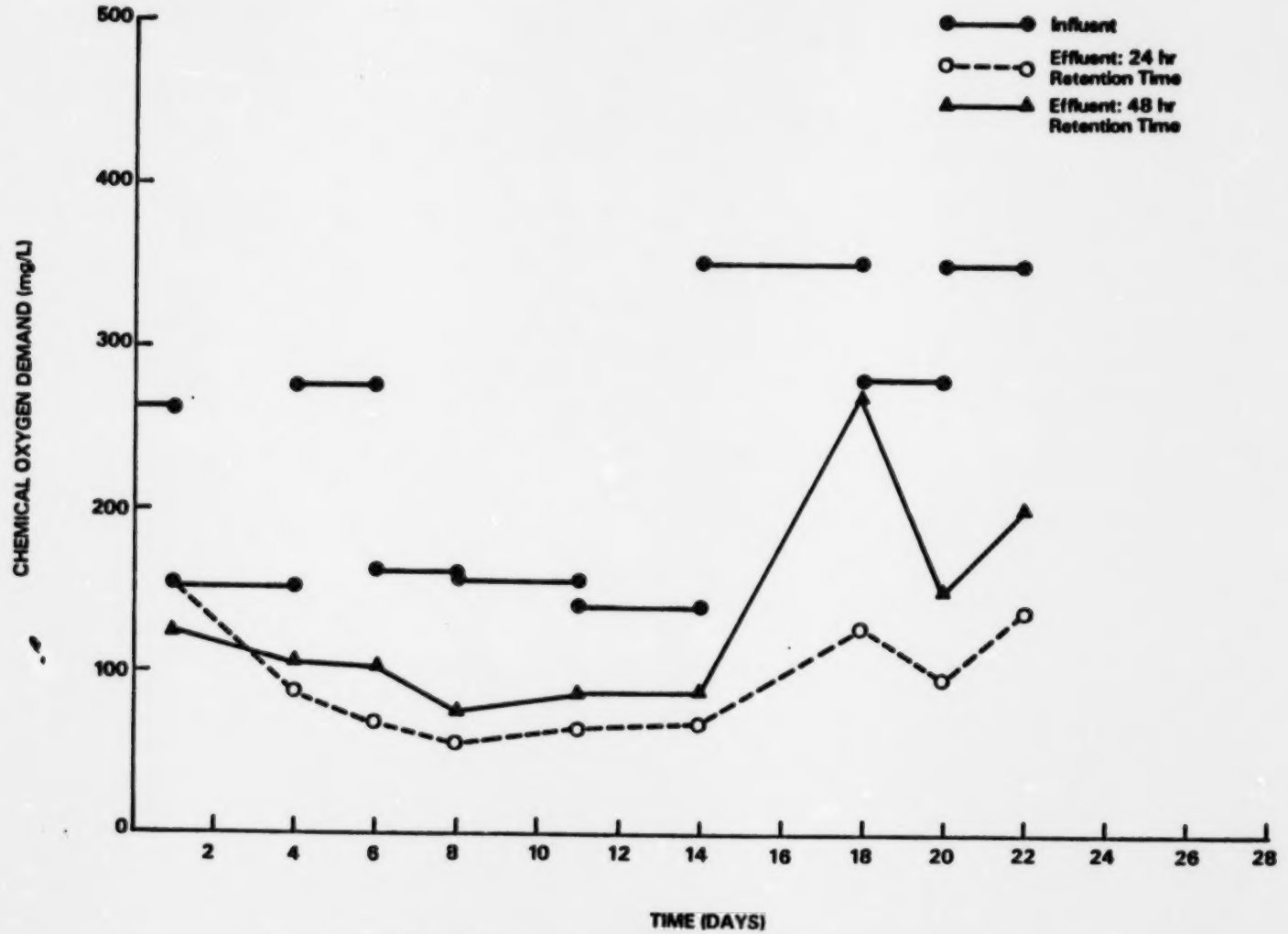


Figure 5. Reduction in chemical oxygen demand in test units.

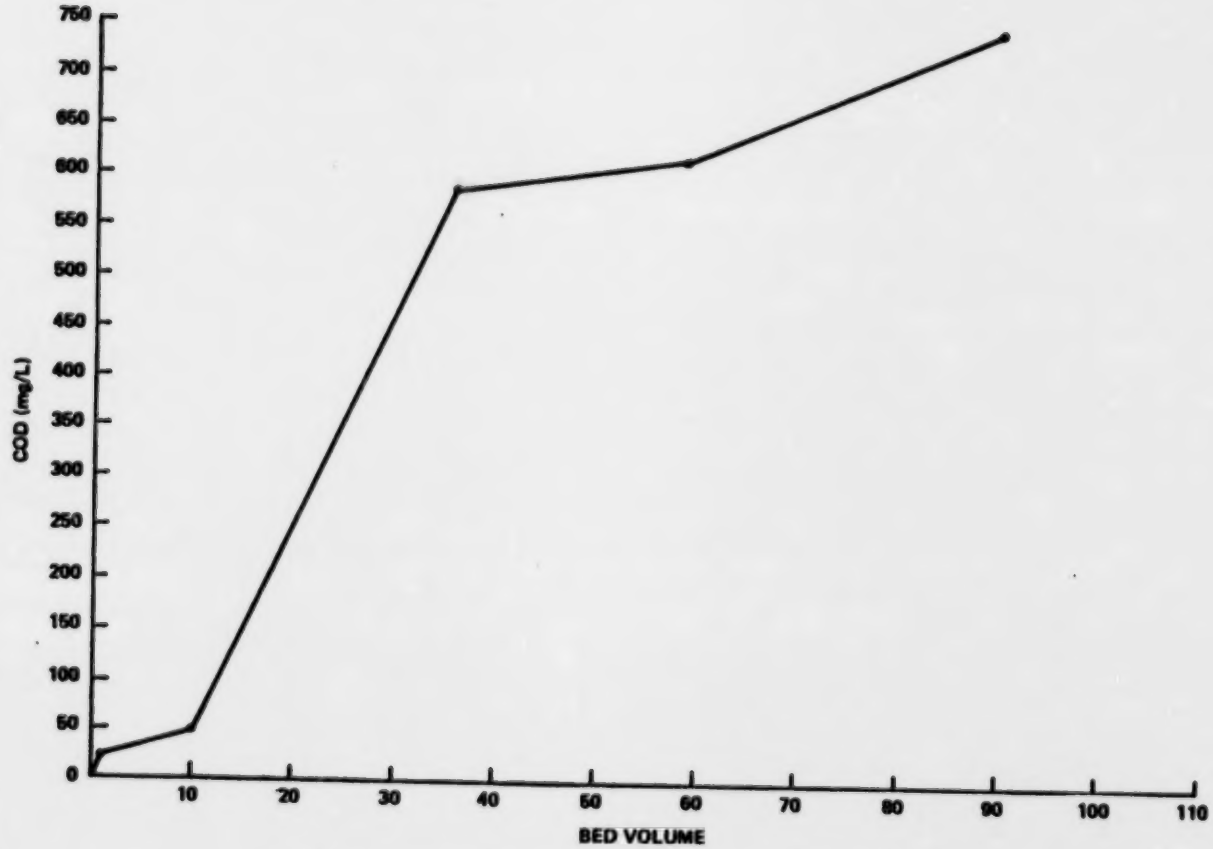


Figure 6. Chemical oxygen demand of various fractions of carbon treated dinoseb-atrazine composite.

The carbon-treated dinoseb-atrazine effluent was composited and combined in a 49:1 ratio with carbon-treated dinoseb supernatant and subjected to biological treatment. It was assumed that the bacterial populations in the activated sludge units used in the previous test were acclimated or resistant to most of the compounds in this pesticide waste. The sludge from the four test units used in the hydroxyatrazine study was settled and combined into two units. MLVSS levels were intially 1700 mg/l in the test units and 2100 mg/L in the controls.

The carbon treated pesticide wastewaters were intially mixed 60% in primary settled municipal wastewater. These wastes were fed to AS units with a 24 hour retention time. 0.4 g of $NaHCO_3$ was added per liter of wastewater to buffer the pH to 7.0-7.5. The pesticide wastewater concentration was increased to 100% in two 20% increments over the subsequent two weeks.

The solids levels in the test units stabilized over the three week testing period. MLVSS levels remained at 1550 mg/L. Oxygen uptake rates in test units were approximately 60% that of the controls (0.12 mg/L/min and 0.19 mg/L/min respectively) and reflect the lower MLVSS levels in the test units.

The COD of the composite carbon treated pesticide wastewaters fed to the AS test units averaged 480 mg/L. The effluent from test units fed a undiluted mixture of these wastes during the final week of the test averaged 56 mg/L (range 41 mg/L to 70 mg/L). However, it was noted that mere exposure of the carbon treated pesticide wastewaters to the open air at 24°C for 24 hours reduced the COD from 480 mg/L to 133 mg/L.

The long retention time of the AS units insured complete nitrification of influent ammonia content. Influent ammonia levels averaged 43.0 mg/L as N in the test units and 23.8 in the controls. No ammonia was detected in any effluent samples (detection limit, 0.5 mg/L).

Biological treatment caused an additional reduction in the phytotoxicity of the pesticide wastewaters. As shown in Table 9 the EC_{50} of the carbon treated wastewaters was between 10 and 100 mL/L. The EC_{50} of the carbon treated wastewater given followup biological treatment was greater the 100 mL/L (Table 10). The reduction in phytotoxity after biological treatment may be a function of ammonia removal. Ammonia is reported to have algicidal effects at concentrations as low as 0.4 mg/L (McKee and Wolf, 1963).

TABLE 9. EFFECT OF CARBON FILTERED WASTEWATERS ON ALGAL GROWTH

Pesticide Wastewater (mL/L)	0.0	0.1	1	10	100
Growth (% of control) on Day 14	100	84	98	106	0.2

TABLE 10. EFFECT OF CARBON FILTERED AND BIOLOGICALLY TREATED WASTEWATER ON ALGAL GROWTH

Pesticide Wastewater (mL/L)	0.01	0.1	1	10	100
Growth (% of control) on Day 14	113	102	93	104	103

DISCUSSION OF RESULTS

Based on the work done in this study the most promising treatment option for the dinoseb and atrazine wastes would involve preliminary carbon filtration followed by biological treatment. Carbon filtration appears fairly selective for the pesticides of interest while allowing more water soluble organic compounds to break through. Carbon treatment is most effectively applied to the most concentrated wastestreams.

The issue of the volatility of the organic compounds associated with this waste should be investigated more closely under pilot conditions to determine whether the major part of the organics is lost in this fashion. When instituting a pilot biological testing program an air stripping control should be run in parallel with the biological units. This air stripping control would consist of a pilot unit run under identical conditions as the biological pilot units but without the biological sludge.

An issue of concern to be answered in a pilot testing program is whether sufficient organics remain available to maintain a healthy sludge in the biological units. Long holding times for the wastewater prior to treatment, long retention times within the treatment units and the aeration necessary for activated sludge processes may reduce degradable organic levels below the optimal feed rates for an activated sludge system. The retention time for any biological treatment system should be investigated to

determine the optimal feed rate. Retention times closer to the typical activated sludge system (6-8 hours) could well provide acceptable treatment levels.

Whether air stripping alone would be a viable treatment alternative would depend on the position taken by regulatory agencies and the possible air emission criteria established for the compounds of interest. From a cost standpoint air stripping alone could provide a cheaper treatment alternative than biological treatment. In addition air stripping at high pH would provide for ammonia removal.

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APPENDIX A

ANALYTICAL PROCEDURE FOR DETERMINATION OF ATRAZINE, DINOSEB AND HYDROXYATRAZINE

The procedure for the analysis of atrazine, dinoseb and hydroxyatrazine involves the separation and quantitation of compounds by high-performance liquid chromatography (HPLC) with a reverse phase column and an ultraviolet absorption detection system.

A modular liquid chromatographic system was used for analyses. The basic system consisted of the following components: 2 M6000 pumps with an M660 solvent programmer and a U6K injector (Waters Assoc.); Model SF 770 variable wavelength detector (Schoeffel Inst.). A reverse phase column packed with Partisil 10 bonded with octadecyl trichlorosilane was employed.

The mobile phase, detector wavelength and detection limit are given in Table A-1 for the compounds analyzed in this study.

TABLE A-1 ANALYTICAL PARAMETERS FOR PESTICIDES OF INTEREST

Compound	Mobile Phase (% CH_3CN in H_2O)	Detector Wavelength (nm)	Minimum Detectable Quantity (ng)	Standard Deviation at 1 mg/L
Atrazine	60%	263	0.05	2.5%
Dinoseb	60%	263	0.01	3.0%
Hydroxyatrazine	25%	230	0.01	2.5%

Flow rate of the mobile phase was 2 mL/min. Sample injection size was 10 µL. All samples were filtered through a 0.45 µ Millipore HA filter prior to analysis.

APPENDIX B

ANALYTICAL PROCEDURES FOR ROUTINE WASTEWATER CHARACTERIZATION

Routine wastewater analyses were conducted according to Standard Methods for the Examination of Water and Wastewater, 14th Edition, (APHA, AWWA, WPCF, 1975).

pH--

pH was determined electrometrically by Method 424.

Chloride--

Chloride was measured by the mercuric nitrate method (Method 408 B).

Acidity--

Acidity, as $CaCO_3$, was determined by Method 402.

Alkalinity--

Alkalinity, as $CaCO_3$, was determined by Method 403.

Nitrogen Forms--

Total Kjeldahl nitrogen was determined after digestion according to Method 42. Ammonia (NH_3-N) was determined by an acidimetric method as described in Sections 418 A and 418 D. Nitrite and nitrate nitrogen (NO_2-N, NO_3-N) were determined by the Devarda's alloy method (419 F).

COD--

Chemical oxygen demand (COD) was determined by Method 508.

Residues--

Suspended solids (SS) were determined by Method 208 D. Total solids (TS) were determined by Method 208 A. Total dissolved solids (TDS) were determined by Method 208 A. Settleable solids were determined by Method 208 F.

the test materials. These authors suggest that, in general practice, the results be based on the growth at 14 days, i.e., as % I_{14} or % S_{14} at a given concentration of the effluent being tested.

Decreased growth, compared to the control, is evidence of an inhibitory effect. The manner in which the test is conducted does not allow determination of whether this inhibition is temporary (algistatic) or permanent (algicidal). Such a determination would require further testing by subculturing into fresh medium free of the test material.

APPENDIX C

PROCEDURES FOR CONDUCTING ACTIVATED SLUDGE TREATABILITY TESTS

For biological treatability studies the bench scale, complete-mix, continuous-feed, activated sludge unit designed by Swisher (1970) was employed (Figure C-1). This unit has an aerator capacity of 0.3 L and a settler capacity of 0.075 L. The unit is made entirely of glass, avoiding the possibility of contamination by organics leaching from the container. Continuous feed to the units was supplied through Teflon tubing by a peristaltic pump to give the nominal retention times as listed in the text.

The units were started with activated sludge from the Hope Valley Treatment Plant, Durham, NC, which treats municipal wastewater. The units were then fed from a reservoir of primary wastewater from the Chapel Hill Treatment Plant. When a steady-state condition was reached, as indicated by consistent effluent quality in terms of COD and mixed liquid suspended solids levels, the feed to the test units was spiked with pesticide wastewater. Control units were fed only primary wastewater.

The pesticide spiked wastewaters were prepared by adding pesticide wastewater to the primary municipal wastewater which had been allowed to settle for a 120 min to simulate primary settling. Routine determinations were made of dissolved oxygen, pH, mixed liquor volatile suspended solids in the aerator and the COD and pesticide concentrations in the influent and effluent. Dissolved oxygen was determined with an oxygen probe (Yellow Springs Instrument Co.).

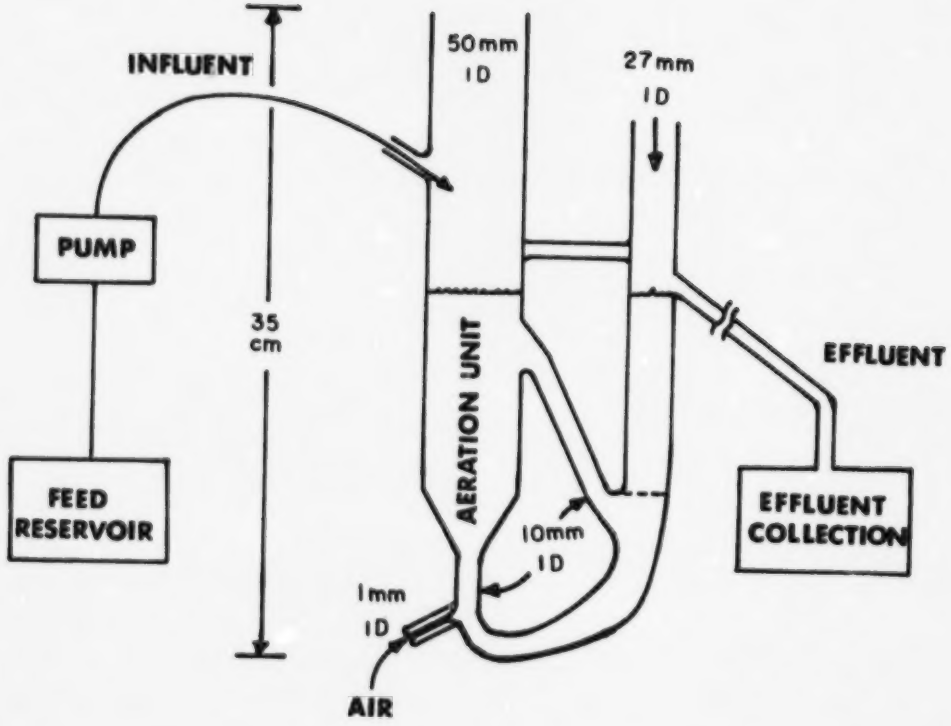

Figure C-1. Diagram of a Swisher activated sludge bench scale unit.

APPENDIX D

PROCEDURES FOR ALGAL ASSAY TESTS

Algal bioassays were conducted according to the freshwater algal assay procedure described in the report The Selenastrum Capricornutum Printz Algal Assay Bottle Test (Miller, Greene, and Shiroyama, 1978). The test alga was Selenastrum capricornutum Printz, obtained from the National Eutrophication Research Program, EPA, Corvallis, Oregon. This test was designed to measure algal response to changes in nutrient concentrations and to determine toxicity or inhibition.

Wastewaters to be tested were filter sterilized through a sterile prewashed membrane filter (Millipore Filter, 0.45 μm pore size). Serial dilutions were then made in sterile algal media to give the appropriate final concentration. Sufficient inoculum was added to produce an initial cell concentration of 10^4 cells/mL.

In each set of experiments, algal growth in the presence of a series of concentrations of the wastewater added to the nutrient medium was compared to algal growth in the nutrient medium alone. Growth was determined by direct counts of the algae during the 10-14 day incubation period. Effect of the wastewater on algal growth was determined in terms of the effect on the cell yield. Direct cell counts were performed by an automated procedure utilizing a Fisher Scientific Model FO 16 particle counter.

The tests were conducted in water bath shakers at 24 $\pm$ 2°C and at approximately 80 oscillations per minute with constant white fluorescent lighting at 4300 lux. Test containers were 250 mL Erlenmeyer Pyrex flasks containing 100 mL of test medium and covered with an inverted Pyrex beaker.

The method of expressing inhibitory or stimulatory effects was that recommended by Miller et al. (1978), i.e., as the percent growth inhibition (I) or stimulation (S), as compared to growth in a control culture without

the test materials. These authors suggest that, in general practice, the results be based on the growth at 14 days, i.e., as % I_{14} or % S_{14} at a given concentration of the effluent being tested.

Decreased growth, compared to the control, is evidence of an inhibitory effect. The manner in which the test is conducted does not allow determination of whether this inhibition is temporary (algistatic) or permanent (algicidal). Such a determination would require further testing by subculturing into fresh medium free of the test material.